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T Hydrates at High Pressures, Part II:

Application of Statistical Mechanics to the Study of the

Hydrates of Methane, Argon, and Nitrogen

by

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ABSTRACT

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The statistical mechanical solid solution theory of van der Waals and Platteeuw has been applied to study the experimentally determined three-phase hydrate-water rich liquid-gas locus of methane, argon, and nitrogen-water up to an upper pressure of 50,000 pisa. The results of calculations show that the solid solution theory can be applied to the hydrates quite well when the caged gas is a spherical molecule but can deviate for slightly non-spherical molecules at high pressure. At higher pressures the hydrate numbers calculated from this theory approached the number of  $5 \frac{3}{4}$  which is based on complete occupation of all the cavities.

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### Theoretical Development

A. Hydrate Structure: The structure of gas hydrates was determined by Von Stackelberg and Muller<sup>15, 16</sup> through the use of X-ray diffraction techniques. Structural arrays capable of fitting these data were formulated by Claussen<sup>2</sup> and Pauling and Marsh<sup>13</sup> who state that all gas hydrates crystallize in either of two cubic structures which have been labelled Structure I and Structure II. The hydrated molecules are situated in cavities formed by a framework of water molecules linked together by hydrogen bonds. The host lattice by itself is thermodynamically unstable, but is stabilized by the inclusion of a second component within the lattice.

The unit cell of Structure I contains 46 water molecules enclosing two types of cavities:

1. Six pentagonal dodecahedra cavities consisting of twenty water molecules each located at the vertices and center of the unit cell.
2. Two tetrakaidecahedra cavities having two opposite hexagonal faces and twelve pentagonal faces serving to connect the regular dodecahedra.

The pentagonal dodecahedra are smaller than the two tetrakaidecahedra, having an average radius of  $3.95 \text{ \AA}$  as compared with  $4.30 \text{ \AA}$  for the tetrakaidecahedra. Thus, if all cavities were filled, the maximum hydrate number for Structure I would be  $46/8$  or  $5 \frac{3}{4}$ .

The unit cell of Structure II is composed of 136 water molecules arranged to form sixteen smaller cavities and eight larger cavities. The smaller cavities are distorted dodecahedra with an average radius of 3.91 Å while the larger cavities are almost spherical with an average radius of 4.73 Å. Structure II is formed only by hydrated molecules which are too large to fit within the cavities of Structure I. The foregoing calculations are concerned with hydrates falling in the Structure I category.

In the previous paper<sup>11</sup>, it was reported that the pressure-temperature projections of methane, argon, and nitrogen hydrates exhibited no detectable abnormality at high pressure. From this, it was expected that the change of the crystal structure of the same hydrates would not occur in the range of pressure studied.

B. Outline of the solid solution theory: The derivation of the solid solution theory of clathrate is given by van der Waals and Platteeuw<sup>18</sup>. The general theory is developed for a lattice former denoted by W which can exist in (1) a metastable modification  $W^\beta$  (empty clathrate lattice), (2) a stable crystalline modification  $W^\alpha$ , and (3) a liquid modification  $W^L$ .

The basic equations which describe the clathrate are:

$$\mu_w = \mu^\beta + kT \sum_i V_i \ln(1 - \sum_K y_{Ki}) \quad (1)$$

$$y_{ki} = C_{ki} f_K / (1 + \sum_j C_{ji} f_j) \quad (2)$$

$$C_{ki} = (1/kT) h_{ki}(T,V) / \phi_K(T) \quad (3)$$

In Equation (1)  $\mu_w$  represents the chemical potential of water, in the hydrate. The term  $\mu_w^B$  represents the chemical potential of water in the empty lattice structure modification. The term  $\nu_i$  denotes the number of cavities of the type  $i$  per molecule of water. For gas hydrates of Structure I  $\nu_1 = 1/23$  and  $\nu_2 = 3/23$ , for those of Structure II  $\nu_1 = 2/17$  and  $\nu_2 = 1/17$ . The term  $y_{ki}$  is the fraction of cavities of type  $i$  occupied by a gas molecule  $K$ . Equation (1) is a generalized form of Raoult's law for a solvent when the solvent-solute interaction is negligible. Equation (2) is equivalent to a Langmuir isotherm for localized adsorption without interaction between the adsorbed molecules.  $f_K$  is the fugacity of solute  $K$  in the hydrate. The term  $C_{ki}$  represents the Langmuir constant. Equation (3) defines the Langmuir constant used in Equation (2). The term  $h_{ki}(T,V)$  represents the molecular partition function of a solute molecule of type  $K$  enclosed in a cavity of type  $i$ . The term  $\phi_K(T)$  is the molecular partition function of solute molecule of type  $K$  with the volume factor removed.  $T$  and  $k$  represent the temperature and Boltzmann constant, respectively.

For a clathrate to exist in equilibrium with the crystalline modification  $W^\alpha$ , or the liquid modification  $W^L$ :

$$\mu_w = \mu_w^\alpha \quad \text{or} \quad \mu_w = \mu_w^L \quad (4)$$

Here  $\mu_w^\alpha$  and  $\mu_w^L$  represent the chemical potentials of crystalline and liquid modifications respectively.  $\mu_w^\alpha$  and  $\mu_w^\beta$  are functions of pressure and temperature alone. However,  $\mu_w^L$  is also dependent on composition.

Letting

$$\Delta\mu(T,P) = \mu_w^\beta - \mu_w^\alpha \quad \text{or} \quad \Delta\mu(T,P) = \mu_w^\beta - \mu_w^L \quad (5)$$

then

$$\sum_i \nu_i \ln(1 - \sum_k y_{ki}) = -\Delta\mu/RT \quad (6)$$

$$\sum_i \nu_i \ln(1 - \sum_k c_{ki} f_k) = \Delta\mu/RT \quad (7)$$

The present treatment deals primarily in detail with the fit of the solid solution theory to the experimental data<sup>11</sup> of the three phase hydrate-water rich liquid-gas curves in the region above the quadruple point.

#### Evaluation of the Cell Partition Function

The general equations for a clathrate contain only the cell partition function  $h_{Ti}$  as an unknown, the evaluation of which allows the prediction of the thermodynamic behavior of clathrates relative to the empty lattice.

The cell partition functions have been evaluated by van der Walls and Platteeuw<sup>18</sup> under the following assumptions.

1. The solute molecules can rotate freely in their cavities.

2. The potential energy of a solute molecule at a distance  $r$  from the center of its cage is given by the spherically symmetrical potential  $\omega(r)$  proposed by Lennard-Jones and Devonshire<sup>10</sup>.

$$h = \phi(T) \exp[-\omega(0)/kT] 2\pi a_i^3 g \quad (8)$$

where the potential energy of the solute molecule at the center of the cage is given by

$$\omega(0) = Z_i \bar{E} [\alpha_i^{-4} - 2\alpha_i^{-2}] \quad (9)$$

and  $g$  is a dimensionless integral given by:

$$g = \int_{\text{cell}} \exp \left\{ Z_i \bar{E} / kT [-L(x)/\alpha_i^4 + 2M(x)/\alpha_i^2] x^{1/2} dx \right\} \quad (10)$$

The functions  $L(x)$  and  $M(x)$  are

$$L(x) = (x^4 + 12x^3 + 25.2x^2 + 12x + 1)/(1-x)^{10} \quad (11)$$

$$M(x) = (1+x)/(1-x)^4 - 1 \quad (12)$$

The constant  $\alpha_i$  is defined as:

$$\alpha_i = (a_i/\bar{\sigma})^3/\sqrt{2} \quad (13)$$

where  $a_i$  is the cell radius.  $\bar{\sigma}$  and  $\bar{E}$  are the distance

and energy parameters for solute-water interaction. The variable of integration is defined as

$$x = (r/a_i)^2 \quad (14)$$

where  $r$  is the distance from the center of the cage. Since the contribution to the partition function from portions of the cell outside the sphere of  $a/2$  is negligible, the integration is carried out between the limits 0 and  $1/4$ . The value of  $Z_i$  is a constant derived from structural considerations.

On substituting Equation (8) into Equation (3), the Langmuir constant  $C_{ki}$  becomes:

$$C_{ki} = (2\pi a_i^3/kT) g_{ki} \exp[-\omega(0)/kT] \quad (15)$$

In order to evaluate Equation (15) for a chosen set of molecular parameters and a temperature, a numerical integration of  $g$  was required. The integration was carried out using Simpson's One-Third Rule.

The constants used in the evaluation of  $C_{ki}$  for hydrates of Structure I are as follows<sup>18</sup>.

$$\begin{array}{lll} Z_1 = 20 & a_1 = 3.95 \text{ \AA} & k = 1.38 \times 10^{-16} \text{ erg/deg} \\ Z_2 = 24 & a_2 = 4.30 \text{ \AA} & \end{array}$$

Thus, if  $\bar{\epsilon}$  and  $\bar{\sigma}$  are known, the Langmuir constant  $C_{ki}$  may be evaluated for a given system.



### Determination of $\bar{E}$ and $\bar{v}$ for Methane

For the solid solution theory to be exact, a unique set of molecular parameters should exist for all data on each gas hydrate.

The set of molecular parameters used throughout the theoretical calculations for methane was derived in the following manner:

Below the quadruple point the physical system is composed of ice, hydrate, and gas in univariant equilibrium. This system admits to a theoretical treatment more readily than the system above the quadruple point which consists of hydrate, gas and aqueous solution. Below the quadruple point, a simplification results because the chemical potential difference between the stable and metastable forms of the lattice former is a function of the system pressure and temperature alone.

From these considerations, it was decided that the force constants for methane should be fitted below the quadruple point where the solid solution theory could be applied exactly. Then these parameters were used to correlate the experimental data above the quadruple point.

Experimental data of Deaton and Frost<sup>5</sup> on the three phase locus, ice-water rich liquid-gas, were used to determine the best set of molecular parameters for methane along the hydrate locus. Using the various sets of the molecular

parameters, fugacities in equilibrium with the hydrate were calculated from Equations (7) and (15) and then compared with the experimental values. In order to solve Equation (7), a numerical calculation was carried out using Newton's method. Thus, the set of molecular parameters which exhibited the least deviation from the data of Deaton and Frost<sup>5</sup> was chosen for use in all subsequent calculations for methane. As shown in Figure 1 the values chosen were  $\bar{E}/R = 158.5$  ( $^{\circ}\text{K}$ ) and  $\bar{\sigma} = 3.08$  ( $\text{\AA}$ ). Figure 1 shows that Equation (7) is so sensitive to  $\bar{E}$  and  $\bar{\sigma}$  that  $\bar{E}$ ,  $\bar{\sigma}$  from published data can not be substituted in Equation (7) directly.

The chemical potential difference between ice and hydrate along the equilibrium curve was calculated from the following equation:

$$d(\Delta\mu/RT) = -(\Delta H/RT^2)dT + (\Delta V/RT)dP \quad (16)$$

This equation holds for any value of  $dP$  and  $dT$ . On the equilibrium curve,

$$dP = (dP/dT)dT \quad (17)$$

Integration of Equation (16) between  $T$  and  $273^{\circ}\text{K}$  along the equilibrium curve gives:

$$\Delta\mu/RT = -\int(\Delta H/RT^2)dT + \int(\Delta V/RT)(dP/dT)dT \quad (18)$$

$$dP/dT = 0.03299 e^{(0.03299T - 5.780)} \quad (19)$$

$$\Delta\mu(273^\circ K, P_{atm}) = 167 + 0.073P \quad (20)$$

where  $\Delta V$  is the difference between molar volume of the  $\alpha$  and  $\beta$  modifications,  $V^\beta - V^\alpha$ . Stackelberg and Muller<sup>16</sup> have determined a value of 3.0 for  $\Delta V$ . Equation (19) was obtained from the data of Deaton and Frost<sup>5</sup>. Equation (20) has been derived by van der Waals and Platteeuw<sup>18</sup>.  $\Delta H$  is the difference between molar heat functions of the  $\alpha$  and  $\beta$  modifications. This value is not known but van der Waals and Platteeuw suggested  $\Delta H \simeq 0$ .

#### The Theoretical Fit to the Gas Hydrate Above the Quadruple Point

In order to fit the experimental data to the solid solution theory for gas hydrates above the quadruple point, the following procedure was adopted.

Initially, a series of Langmuir constants were calculated for the methane-water rich liquid-hydrate system and shown in Figure 2.

Next, the assumption was made that the chemical potential of the water in contact with the equilibrium hydrate could be estimated from an ideal solution relationship. With the assumption, the chemical potential of the lattice former can be written as

$$\mu_w^L = (\mu_w^L)^* + RT \ln X_w \quad (21)$$

where  $(\mu_w^L)^*$  is a function of pressure and temperature only and  $X_w$  is the mole fraction of water in the water-rich liquid phase.

Then the chemical potential difference can be expressed by:

$$\begin{aligned}\Delta\mu_w &= \mu_w^\beta - \mu_w^L \\ &= \mu_w^\beta - (\mu_w^L)^* - RT \ln X_w \\ &= \Delta\mu'_w - RT \ln X_w\end{aligned}\quad (22)$$

That is, the chemical potential difference  $\Delta\mu'_w$  is a function of pressure and temperature alone.

Combining Equations (7) and (22) gives:

$$\Delta\mu' = RT \{ \nu_1 \ln(1 + C_{K1} f_K) + \nu_2 \ln(1 + C_{K2} f_K) + \ln X_w \} \quad (23)$$

The pressure and temperature effects on this chemical potential then becomes:

$$d(\Delta\mu'/RT) = -(\Delta H'/RT^2)dT + (\Delta V'/RT)dP \quad (24)$$

where  $\Delta H'$  denotes the difference between molar heat functions and  $\Delta V'$  the difference between the molar volumes of the  $\beta$  and  $L$  modifications. The value of  $\Delta V'$  is  $4.6^{16}$ . It is doubtful that  $\Delta V'$  will retain this constancy at higher pressure, but it was assumed that the change of  $\Delta V'$  is negligible, because of a lack of data on the effect of pressure.

Integrating Equation (24) along the equilibrium curve gives:

$$\Delta\mu'/RT = - \int (\Delta H'/RT^2) dT + \int (\Delta V'/RT) (dP/dT) dT \quad (25)$$

Anticipating that  $\Delta H'$  takes the same form as the heat function difference between water and ice, one can write

$$\Delta H' = -\lambda e^{\gamma T} \quad (26)$$

Substituting (26) into (25) and equating it with (23) gives:

$$[V_1 \ln(1+C_{K1}f) + V_2 \ln(1+C_{K2}f_K) + \ln X_w]_{T_1}^{T_2} = - \int_{T_1}^{T_2} \lambda e^{\gamma T} / RT^2 dT + \int_{T_1}^{T_2} (\Delta V'/RT) (dP/dT) dT \quad (27)$$

The solubility data of Culberson and McKetta<sup>4</sup> for methane in water was used to obtain the composition of water in the liquid phase. The methane P-T projection of the data of Deaton and Frost is linear between 32 and 70° F when plotted in semi-log scale and in this region can be expressed as:

$$dP/dT = 2.635 \times 10^{-12} e^{0.101097 T} \quad (28)$$

If this expression is substituted in Equation (27) then  $\lambda$  and  $\gamma$  can be determined. The values of  $\lambda$  and  $\gamma$  determined numerically were 16.7 and 0.016 respectively. It is noted that the values were very close to those for the heat function difference between ice and water of 17.1 and 0.0162, which were calculated from the data of Bridgman<sup>1</sup>. From this result it was concluded that the difference in enthalpy between the  $\beta$ -lattice and ice must be small.

At constant temperature the pressure effect on the chemical potential difference  $\Delta\mu'$  becomes:

$$(\partial(\Delta\mu')/\partial P)_T = \Delta V' \quad (29)$$

Integrating Equation (29) at constant temperature gives:

$$\Delta\mu' = \Delta\mu'_0 + \Delta V (P - P_0) \quad (30)$$

If  $\Delta\mu'_0$  and  $P$  of methane are used for the reference values  $\Delta\mu'_0$  and  $P_0$ , then the chemical potential difference for argon and nitrogen can be calculated.

$$\Delta\mu' = \Delta\mu'_{\text{CH}_4} + 7.573 \times 10^{-3} (P - P_{\text{CH}_4}) \quad (31)$$

Here the unit of chemical potential and pressure are cal/mol and psia respectively.

Equations (23) and (30) should be equivalent.

Each set of molecular parameters for argon and nitrogen was adjusted at 280° K so that the chemical potential difference calculated by Equation (23) might agree exactly with that calculated from Equation (31). The resulting  $\bar{\epsilon}/k$  and  $\bar{\sigma}$  were 142 (°K), 2.99 (Å) for argon-water and 123 (°K), 3.027 (Å) for nitrogen-water. Using these values,  $C_{KL}$  of argon and nitrogen were calculated and are shown in Figures 3 and 4.

As a test of the theory, Equation (31) was used to calculate the remaining values of the chemical potential differences over the pressure range 1,400 to 50,000 psia for argon and 5,000 to 50,000 psia for nitrogen. The values derived in this way were compared with the right hand side of Equation (23).

These are shown in Table 1, 2, and 3 and in Figure 5. The results of these calculations showed that the solid solution theory may be applied to predict the hydrate-water rich liquid-gas equilibrium loci when gas is a spherical molecule. Here the solubilities of argon and nitrogen in water were extrapolated or interpolated from the data of Seidel and Link<sup>14</sup>, and Krichevsky and Kasarnovsky<sup>9</sup>.

At higher pressures nitrogen showed some deviation between Equations (23) and (31). This somewhat poorer agreement between the two methods can be explained as follows; on applying the L-J-D potential to this theory, the assumption is made that the gas molecules encaged in the hydrate are spherical. This assumption applies equally well to argon and methane, both essentially spherical molecules. However, nitrogen, being non-spherical in shape, does not strictly conform to this theoretical treatment.

Very near the quadruple point, both argon and nitrogen showed slight deviation between Equations (23) and (31) but the reason is not apparent to the authors.

The elimination of  $\Delta\mu'$  from Equations (23) and (31) for a given temperature leads to the evaluation of a single pressure for hydrate formation provided fugacity data on the gas are available. A comparison between this calculated and experimental hydrate formation pressure for nitrogen is shown in Figure 9. It is evident that a given deviation in the  $\Delta\mu'$

leads to a correspondingly greater deviation in the calculated and experimental pressure. However, since the  $\Delta\mu'$  for the argon hydrate obtained by Equations (23) and (31) are identical, the calculated and experimental pressure will be the same.

The hydrate numbers  $n$  were calculated by the following equation and are shown in Table 1, 2, and 3 and in Figure 6.

$$n = 23 / \{ C_{K1} f_K / (1 + C_{K1} f_K) + 3 C_{K2} f_K / (1 + C_{K2} f_K) \} \quad (32)$$

At higher pressure it was shown that the hydrate numbers approach the maximum hydrate number of  $5 \frac{3}{4}$ .

The potential fields within argon hydrate cages were determined by the Lennard-Johns-Devonshire method<sup>10</sup> and are shown in Figure 7. In the large cavities, the minimum point of potential energy is not situated in the center.

#### Estimation of $\epsilon_K$ and $\sigma_K$ for Methane, Argon, and Nitrogen

In the previous sections, the sets of molecular parameters  $\bar{\epsilon}$  and  $\bar{\sigma}$  for methane, argon, and nitrogen were determined. The following empirical combining laws which relate the force constants between unlike molecules were used to calculate the force constants for the pure solute K.

$$\bar{\sigma} = 1/2 (\sigma_w + \sigma_K) \quad (33)$$

$$\bar{\epsilon} = (\epsilon_w \epsilon_K)^{1/2} \quad (34)$$

Here if the value of  $\sigma = 1.25 \text{ \AA}$  which corresponds to Pauling's



van der Waals radius of  $1.40 \text{ \AA}$  for a covalently bound oxygen atom<sup>12</sup>, is adopted as the distance parameter of the wall of the hydrate cage,  $\sigma_K$  for the pure solute K can be estimated. From the value of  $\epsilon_w$  the energy parameter  $\epsilon_K$  for pure solute K also can be estimated. But  $\epsilon_w$  is unknown and cannot be calculated theoretically. So the value of  $\epsilon_w/R = 169^\circ \text{ K}$  was estimated from Equation (34) by using a value of  $\epsilon_K/R = 119.8^\circ \text{ K}$  for argon obtained from second virial coefficient data. Using this value, the energy parameters  $\epsilon_K$  for methane and nitrogen can be estimated.

The force constants obtained are compared in Table 4 with the values<sup>8</sup> of molecular parameters derived from viscosity and virial data for those gases.

#### Determination of Heats of Formation of Methane, Argon, and Nitrogen Hydrates

The heats of formation of hydrates are calculated by the Clausius-Clapeyron equation:

$$dP/dT = \Delta H''/T \cdot \Delta V'' \quad (35)$$

which is a thermodynamic identity valid for all univariant equilibria, no matter how the compositions of the phases change along the equilibrium line. The double primed quantities  $\Delta H''$  and  $\Delta V''$  should be the differences of partial molal quantities, but in this case it was assumed that  $\Delta H''$  and  $\Delta V''$  approximate the changes in heat function and total volume when one mole of

hydrate is formed from  $n$  moles of pure water and one mole of pure gaseous K.

The data points plotted as  $\log P$  versus absolute temperature were fitted approximately along several straight lines<sup>11</sup>. The lines may be represented by an equation of the form:

$$\log P = A + BT \quad (36)$$

Equation (36) lends itself readily to the differentiation required to solve for the heat of formation of the hydrate.

The mathematical analysis followed in calculating the heats of formation above the quadruple point from the data shown in a previous report<sup>11</sup> is

$$\Delta H'' = T \Delta V'' dP/dT \quad (37)$$

$$dP/dT = 2.303 \cdot B \cdot P \quad (38)$$

$$\Delta H'' = 2.303 B \cdot T \cdot P \cdot \Delta V'' \quad (39)$$

The slopes of equilibrium lines  $B$  were obtained from the previous report<sup>11</sup> and the volume of the gas under investigation at  $T$  and  $P$  of interest here was obtained from thermodynamical tables of Din<sup>6, 7, 17</sup>.

At higher pressure, the difference between the volume of hydrates resulting from the hydrate-forming reaction and that of the water combined with a mole of the gas is not negligible compared with the volume of one mole of the gases. This difference was obtained by  $n \cdot \Delta V'$  assuming that at higher pressures the volumes of hydrates and water are constant.

The heat of formation of the hydrates may be calculated from Equation (39) by using the values of B and  $\Delta V''$ . The values calculated are given in Table 5.

The heat of formation of the hydrates also may be calculated numerically by the following equations assuming that reaction gases are perfect.

$$\Delta H'' = n \cdot N \sum v_i y_i \{ z \epsilon [-2(1 + g_m/g) \alpha^{-2} + (1 + g_l/g) \alpha^{-4}] \} + P \cdot \Delta V'' - 16.7 e^{0.016 T} \quad (40)$$

where N is Avogadro's number and the functions  $g_l$  and  $g_m$  are defined by

$$g_l = \int_0^{1/4} x^{1/2} l(x) \exp \{ z \epsilon / kT [-l(x)/\alpha^4 + 2m(x)/\alpha^2] \} dx \quad (41)$$

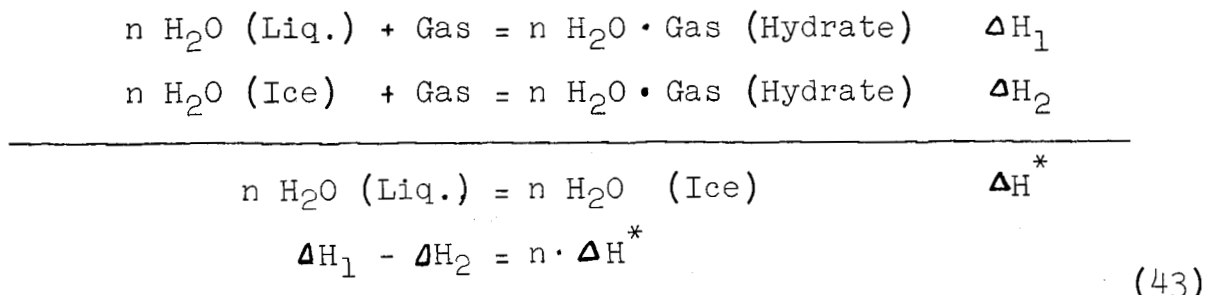
$$g_m = \int_0^{1/4} x^{1/2} m(x) \exp \{ z \epsilon / kT [-l(x)/\alpha^4 + 2m(x)/\alpha^2] \} dx \quad (42)$$

The values calculated by Equation (40) are compared with those obtained from Equation (39) in Table 5. The agreement between two calculations are comparable but not exact owing to the assumptions involved in Equation (40)

#### Prediction of P-T Projection of Nitrogen Hydrate Below The Quadruple Point

At the quadruple point, the differences in the heats of formation of the hydrate from liquid water and from ice will be equal to the heat of fusion of the number of moles of water

combined in a mole of hydrate, as shown by the following:



The heats of formation of hydrate can be calculated by Equation (39) and the hydrate number also is known. Therefore, the slope of equilibrium line below the quadruple point  $B_2$  can be calculated by the following equation:

$$B_2 = 1/\Delta V_2'' (B_1 \Delta V_1'' - n \Delta H^* / 2.303 P \cdot T) \tag{44}$$

where  $\Delta H^*$  is the heat of fusion of water.  $B_1$  is the slope of equilibrium line above the quadruple point.  $\Delta V_1''$  and  $\Delta V_2''$  are the changes in volume of the sum of the reacting substances above and below the quadruple point, respectively.  $B_2$  of nitrogen hydrate was calculated and is compared with the experimental points of Cleef and Diepen<sup>3</sup> in Figure 8. Though the calculated line showed the discontinuity at the quadruple point, the experimental points below the quadruple point fall on an extension of the equilibrium line above the quadruple point.

It is felt that the experimental points reported in reference 3 represent metastable equilibrium gas-hydrate-water rather than the true equilibrium state of gas-hydrate-ice.

### Conclusions

The statistical mechanics solid solution theory of van der Waals and Platteeuw combined with classical thermodynamical principles have been applied to study the conditions for equilibrium for hydrate formation in the methane water, argon-water, and nitrogen-water systems above the quadruple point in excess of 3000 atmospheres. The heat function difference between water and  $\beta$ -modification has been determined by using the Data of Deaton and Frost<sup>5</sup> and it was found that this function is very close to that between ice and water.

Then it was found that the chemical potential difference between the empty hydrate lattice and the pure liquid water,  $\Delta\mu' = \mu_w^\beta - (\mu_w^L)^*$  for argon and nitrogen hydrates calculated by two methods; the chemical potential difference for methane and the isothermal effect of pressure on the chemical potential difference, Equation (31) and the solid solution theory, were in close agreement. While the agreement between the chemical potential difference calculated by the two methods were throughout the entire pressure range studied in the case of argon hydrate, the nitrogen hydrates showed some deviation at the highest pressure studied. The discrepancy is believed to be caused by the slightly non-spherical nature of the nitrogen molecule.

At higher pressure, it was shown that the hydrate numbers approached the maximum hydrate number for Structure I hydrates of  $5 \frac{3}{4}$ .

Using the simple mixing rules given by Equations (33) and (34) and  $\sigma_w$  of  $1.25 \text{ \AA}^{12}$  and  $\epsilon_w/k = 169^\circ \text{ K}$  the Lennard-Jones-Devonshire force constants for methane, argon, and nitrogen have been determined and found to be in essential agreement with the force constants predicted from second virial and viscosity data, again pointing to the essential validity of the theory.

The heat of formation for the hydrates calculated from the Clausius-Clapeyron Equation was found to be in essential agreement with the values predicted by the solid solution model.

The calculated heat of formation for the nitrogen hydrate and its hydrate number on the ice point for the nitrogen-water system has been used as a basis for predicting the gas-ice-hydrate locus below the quadruple point and as a basis for the criticism of reported experimental data points for the same<sup>2</sup>.

The solid solution theory together with classical thermodynamics principles has provided a means of studying the required conditions for hydrate formation above the quadruple point for essentially spherical molecules. It will later be shown that the calculation procedures can be extended to systems comprised of mixtures of essentially spherical molecules and water in the hydrate region above the quadruple point.

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## NOMENCLATURE

$a_i$	cell radius
$A, B$	constant in Equation (34)
$C_{K_i}$	Langmuir constant
$f_K$	fugacity of solute K in the hydrate
$g$	function defined by Equation (10)
$g_l$	function defined by Equation (39)
$g_m$	function defined by Equation (40)
$h_{K_i}(T,V)$	molecular partition function
$\Delta H$	molar enthalpy difference
$k$	Boltzmann constant
$n$	hydrate number
$P$	pressure
$r$	radial position
$R$	gas constant
$T$	temperature
$\Delta V$	molar volume difference
$W$	lattice former (water)
$X_w$	mole fraction of water in the water-rich liquid phase
$x$	$(r/a_i)^2$
$y_{K_i}$	fraction of cavities of type i occupied by a gas molecule K
$Z_i$	structural constant

Greek Letter

$\alpha_i$	$(a_i/\sigma)^3/\sqrt{2}$
$\lambda, \delta$	constants in Equation (26)
$\epsilon, \sigma$	energy and distance parameters in the Lennard-Jones-Devonshire potential
$\nu_i$	number of cavities of the type i per mole of water
$\mu$	chemical potential
$\phi_K(T)$	molecular partition function of a solute molecule K with the volume factor removed
$\omega(r)$	Lennard-Jones-Devonshire potential



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Table 1

Chemical Potential and Hydrate Number of  
Methane Hydrate at Various Pressures

	P		T	f	C		$\Delta\mu$	$\Delta\mu'$	n
	(psi)	(atm)	(°K)	(atm)	(1/atm)	(1/atm)	(cal)	(cal)	
1)	382	26.0	273.1	24.5	0.2028	0.2175	172.8	172.3	6.85
2)	1000	68.0	282.9	59.2	0.1525	0.1690	232.0	231.1	6.34
3)	2000	136.1	289.0	106.2	0.1285	0.1450	276.5	275.1	6.13
4)	3000	204.1	292.3	148.3	0.1173	0.1332	303.2	301.4	6.05
5)	4000	272.1	294.4	191.0	0.1099	0.1257	324.1	322.0	6.00
6)	5000	340.1	296.2	237.2	0.1046	0.1203	343.1	340.9	5.97
7)	6000	408.2	297.5	286.2	0.1006	0.1166	359.9	357.5	5.93
8)	7000	476.2	299.0	344.0	0.0970	0.1130	376.9	374.4	5.89
9)	8000	544.2	300.3	409.9	0.0950	0.1110	394.4	391.7	5.88
10)	9000	612.2	301.4	476.2	0.0927	0.1087	408.8	406.0	5.87
11)	10000	690.3	302.3	558.0	0.0908	0.1064	424.1	421.1	5.84
12)	12000	816.3	303.8	732.2	0.0861	0.1010	448.9	445.8	5.83
13)	15000	1020.4	306.1	1106.1	0.0810	0.0960	489.9	486.4	5.81

Table 2

Chemical Potential and Hydrate Number of  
Argon Hydrate at Various Pressures

	P		T	f	C	C	$\Delta\mu$	$\Delta\mu'$	n
	(psi)	(atm)	(°K)	(atm)	(1/atm)	(1/atm)	(cal)	(cal)	
1)	1402	95.4	273.1	88.0	0.06423	0.07344	186.9	185.1	6.67
2)	1500	102.0	274.1	94.0	0.06225	0.07150	190.7	188.8	6.64
3)	2000	136.1	277.5	122.5	0.05750	0.06640	208.9	206.9	6.49
4)	3000	204.1	281.4	180.0	0.05222	0.06105	237.9	235.7	6.29
5)	4000	271.1	283.7	237.5	0.04945	0.05810	260.2	257.9	6.18
6)	5000	340.1	285.5	298.0	0.04735	0.05595	279.3	276.9	6.13
7)	6000	408.2	287.0	361	0.04568	0.05420	295.7	293.3	6.06
8)	7000	476.2	288.3	435	0.04435	0.05280	312.2	309.7	6.01
9)	8000	544.2	289.4	508	0.04330	0.05165	325.5	322.9	5.98
10)	9000	612.2	290.4	585	0.04230	0.05061	338.8	336.2	5.97
11)	10000	690.3	291.2	689	0.04150	0.04980	354.0	351.3	5.93
12)	20500	1394.5	297.0	2275	0.03655	0.04445	469.7	466.8	5.81
13)	30000	2040.8	300.0	5600	0.03426	0.04193	561.0	557.9	5.78
14)	50000	3401.3	303.9	30000	0.03160	0.3900	736.2	733.0	5.76

Table 3

Chemical Potential and Hydrate Number of  
Nitrogen Hydrate at Various Pressures

	P		T	f	C	C	$\Delta\mu$	$\Delta\mu'$	n
	(psi)	(atm)	(°K)	(atm)	(1/atm)	(1/atm)	(cal)	(cal)	
1)	2370	161.2	273.1	155.7	0.03262	0.04172	185.1	184.1	6.69
2)	3000	204.1	275.6	199.6	0.03070	0.03951	202.7	201.5	6.53
3)	4000	272.1	278.5	273.4	0.02880	0.03822	228.5	227.0	6.34
4)	5000	340.1	280.6	353.7	0.02750	0.03697	249.7	248.0	6.23
5)	6000	408.2	282.3	443.8	0.02651	0.03460	266.3	264.4	6.15
6)	7000	476.2	284.0	547.6	0.02553	0.03350	284.3	282.1	6.09
7)	8000	544.2	285.3	658.1	0.02482	0.03270	300.3	298.0	6.04
8)	9000	612.2	286.6	785.7	0.02415	0.03190	316.1	313.7	6.00
9)	10000	690.3	287.6	926.5	0.02365	0.03130	331.2	328.5	5.97
10)	15000	1020.4	292.0	1937	0.02160	0.02881	400.3	396.7	5.86
11)	20000	1360.5	295.2	3600	0.02028	0.02720	461.1	457.0	5.81
12)	30000	2040.8	300.0	11200	0.01842	0.02498	576.5	571.2	5.77
13)	40000	2721.0	303.3	30106	0.01725	0.02372	680.3	674.2	5.76
14)	50000	3401.3	306.1	88000	0.01635	0.02250	793.5	786.8	5.75

Table 4

Comparison of Molecular Parameters from Virial,  
Viscosity<sup>8</sup>, and Hydrate Data (this work)

Substance	Method	$\epsilon/k$	$\sigma$
Methane	Viscosity	137	3.822
	Viscosity	144	3.796
	Virial	148.2	3.817
	Hydrate	148.6	3.66
Argon	Viscosity	124	3.418
	Viscosity	116	3.465
	Virial	119.8	3.405
	Virial	122	3.40
	Hydrate	119.8*	3.48
Nitrogen	Viscosity	91.5	3.681
	Viscosity	79.8	3.749
	Virial	95.05	3.698
	Virial	95.9	3.71
	Hydrate	89.5	3.55

\* Taken from reference 8

Table 5

Comparison of Heats of Formation of Hydrates from  
Clausius-Clapeyron Equation and from Solid Solution Theory

Press.	<u>Methane</u>		<u>Argon</u>		<u>Nitrogen</u>	
	B.T.U./lb mol		B.T.U./lb mol		B.T.U./lb mol	
	Eq.(37)	Eq.(38)	Eq.(37)	Eq.(38)	Eq.(37)	Eq.(38)
2000	24700	22000	21100	19800	-----	-----
4000	26000	22400	22100	21900	20400	21600
6000	26800	24700	22600	21000	20900	21300
8000	27300	24300	23000	21200	21400	22200
10000	27800	24300	23400	21100	21700	24000



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Hydrate Formation Pressure for Nitrogen

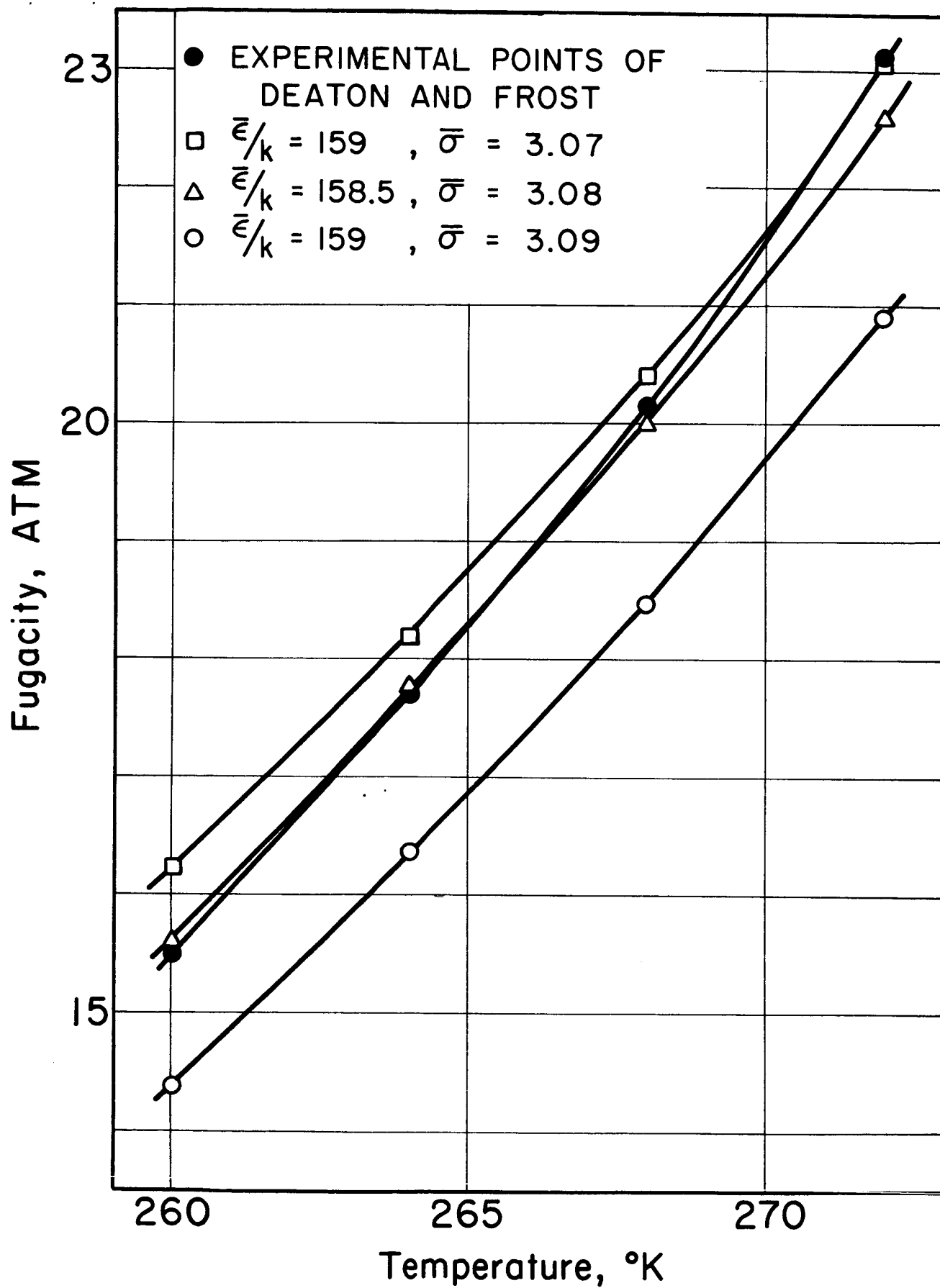


FIG. 1- THEORETICAL FIT BELOW ICE POINT FOR METHANE

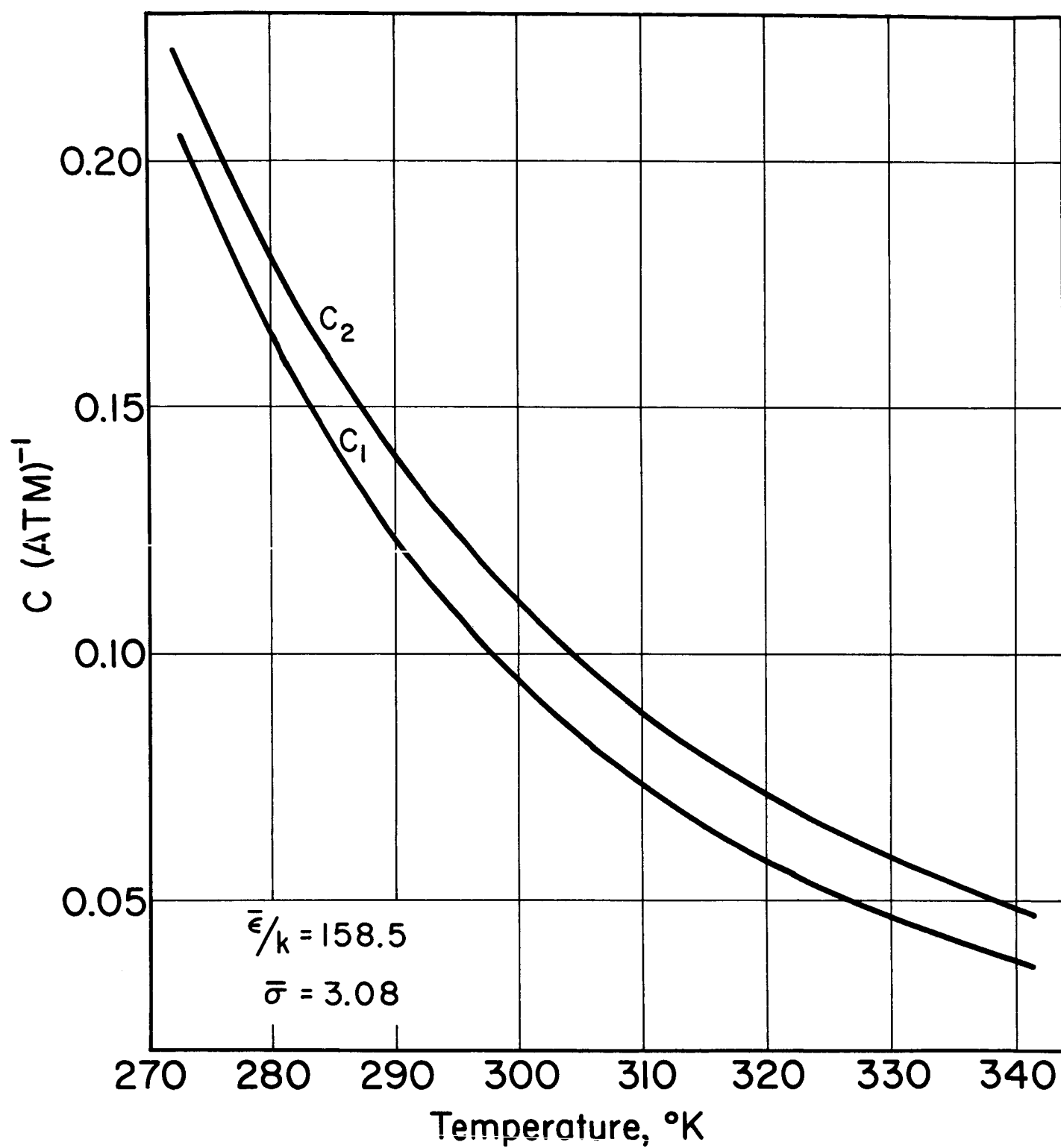


FIG. 2-LANGMUIR CONSTANT for METHANE

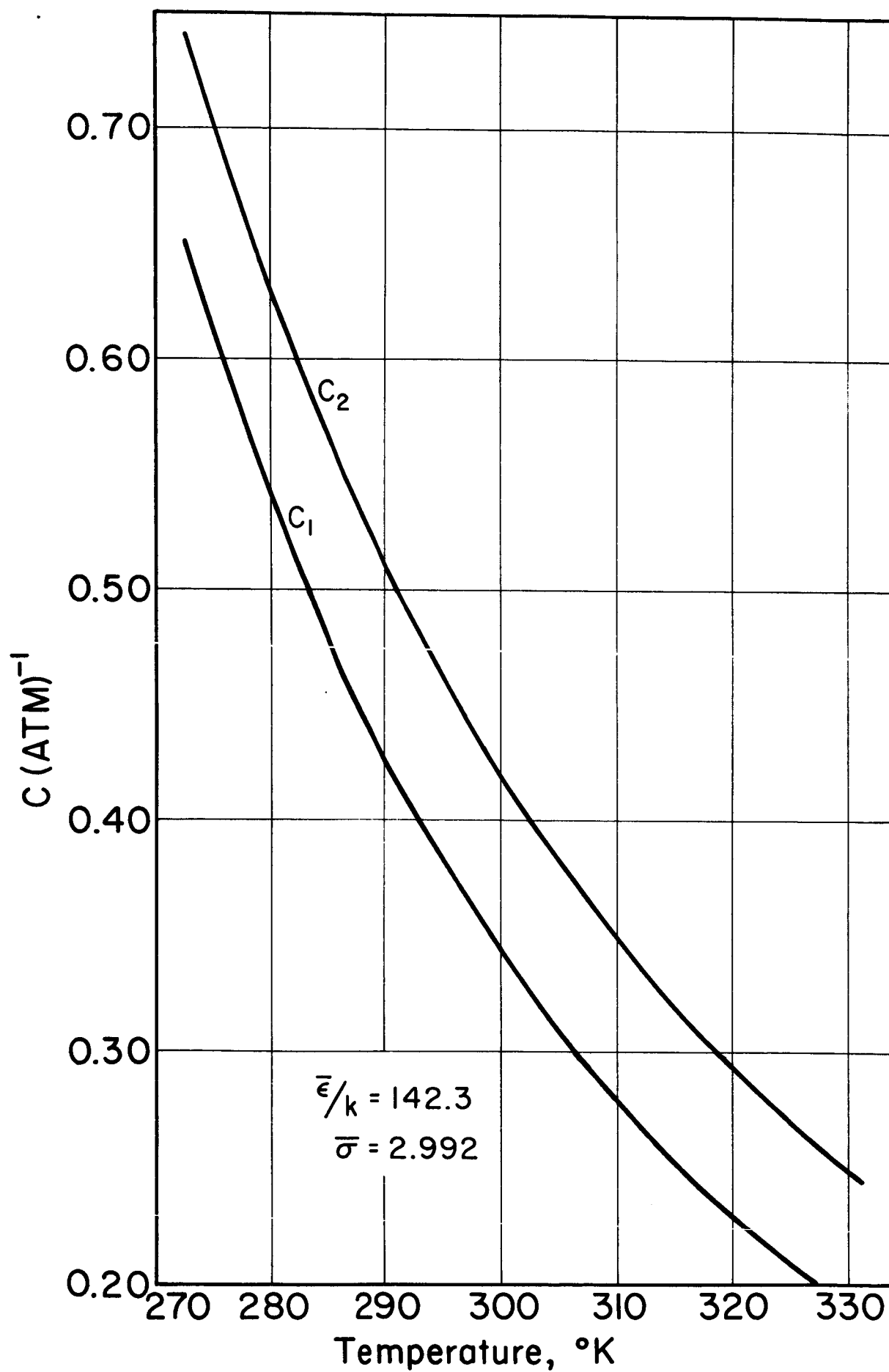
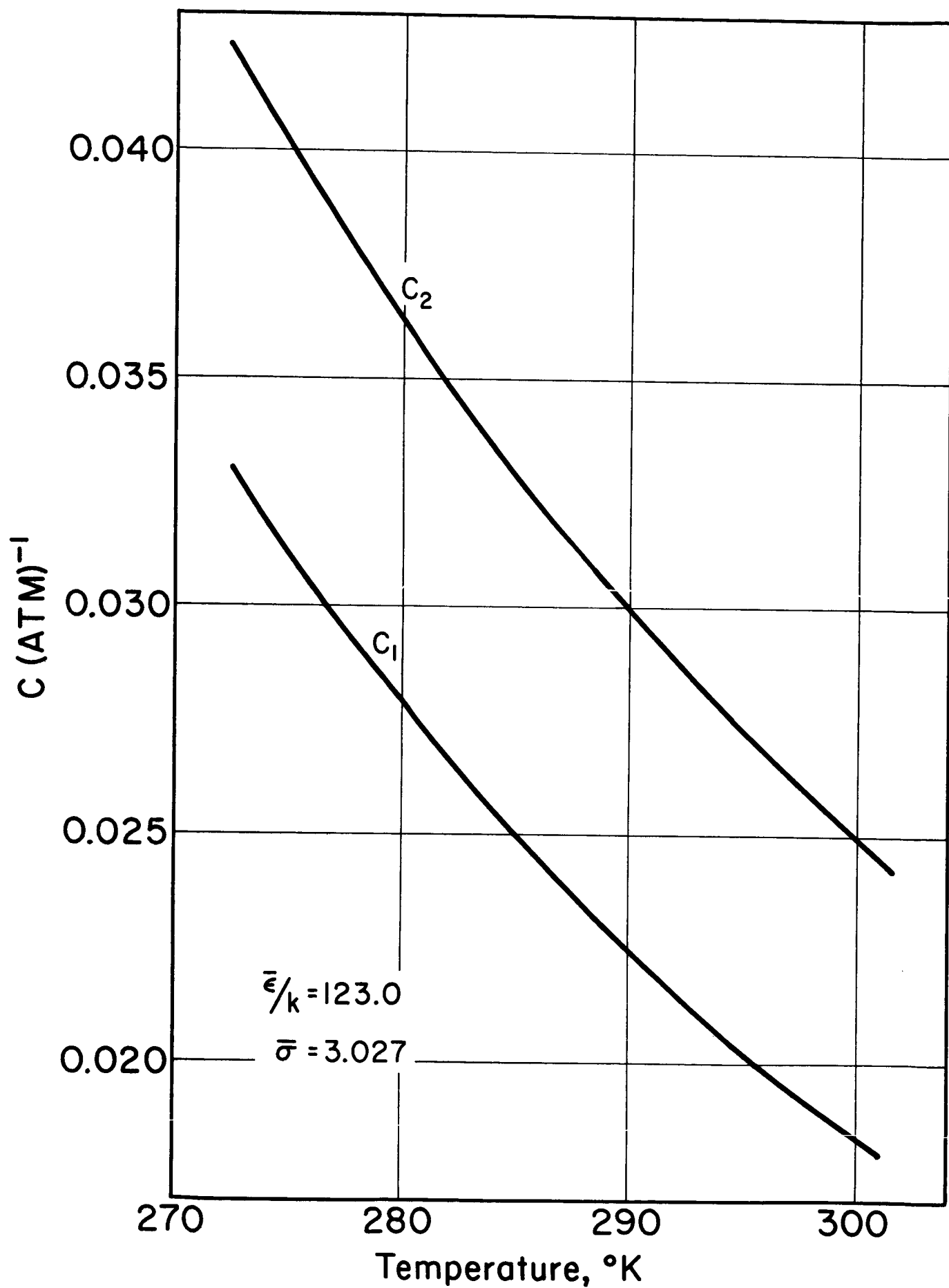


FIG. 3-LANGMUIR CONSTANT for ARGON



**FIG. 4 - LANGMUIR CONSTANT for NITROGEN**

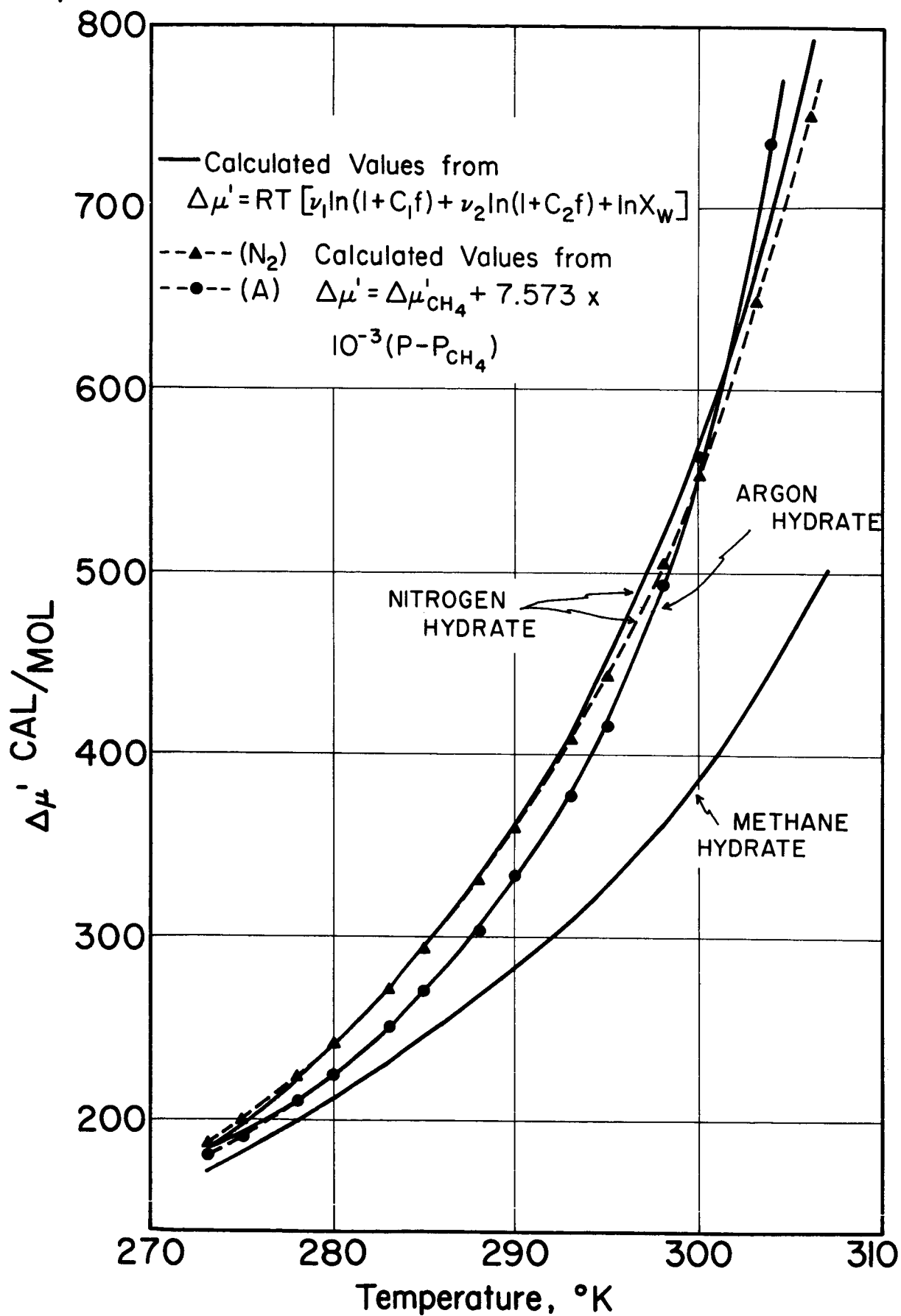
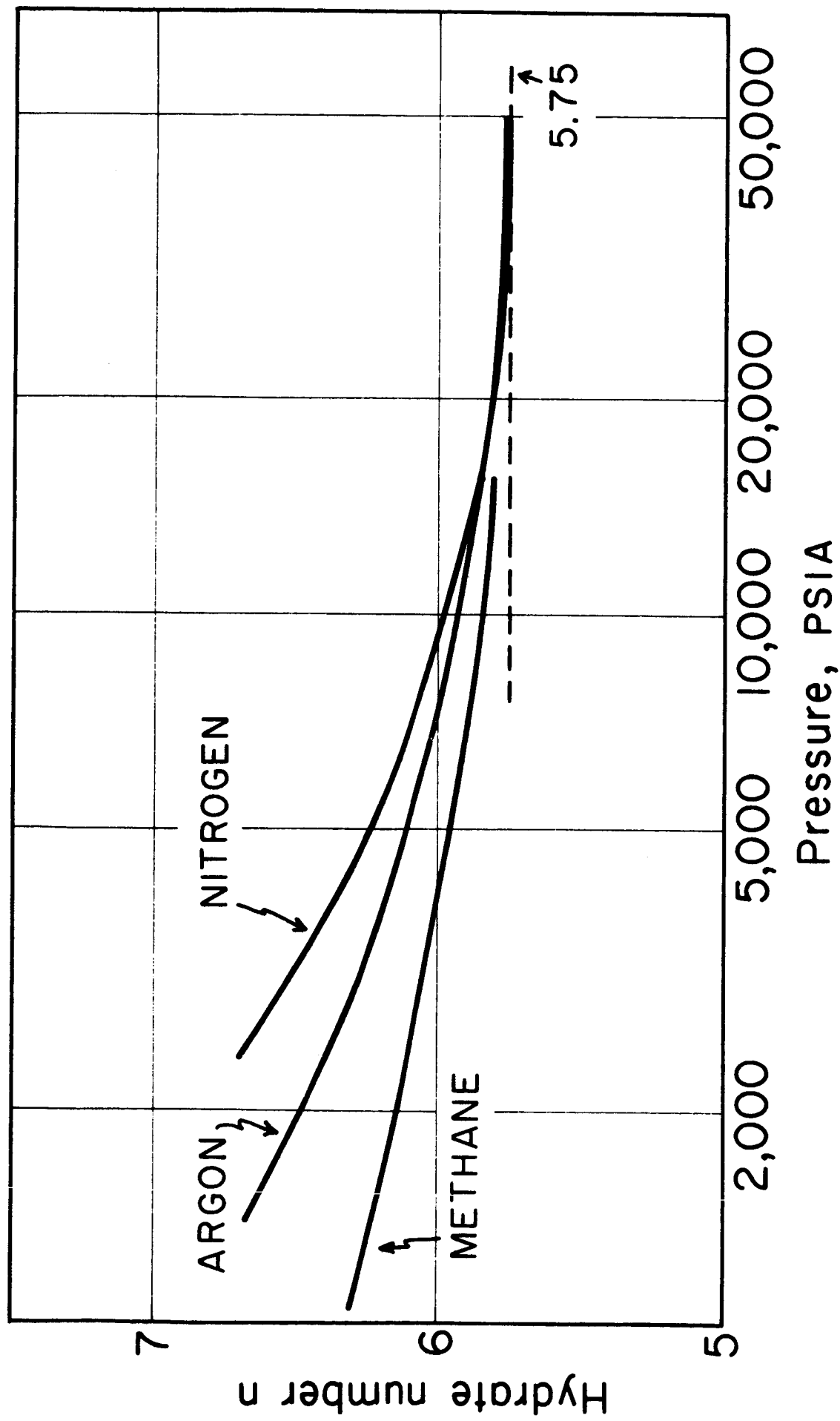


FIG. 5—CHEMICAL POTENTIALS for METHANE, ARGON & NITROGEN above ICE POINT



**FIG. 6 - VARIATION OF HYDRATE NUMBERS WITH PRESSURE**

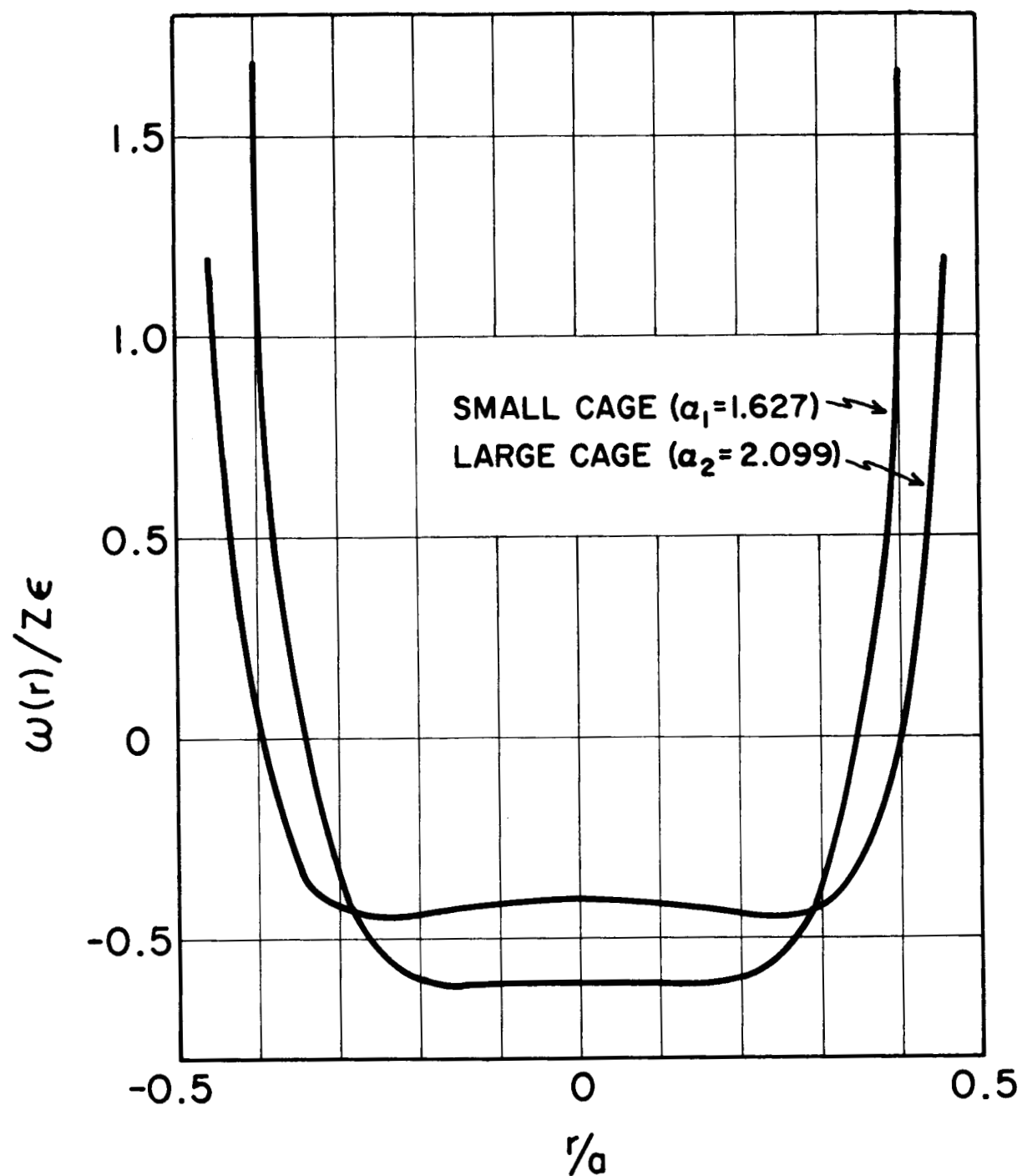
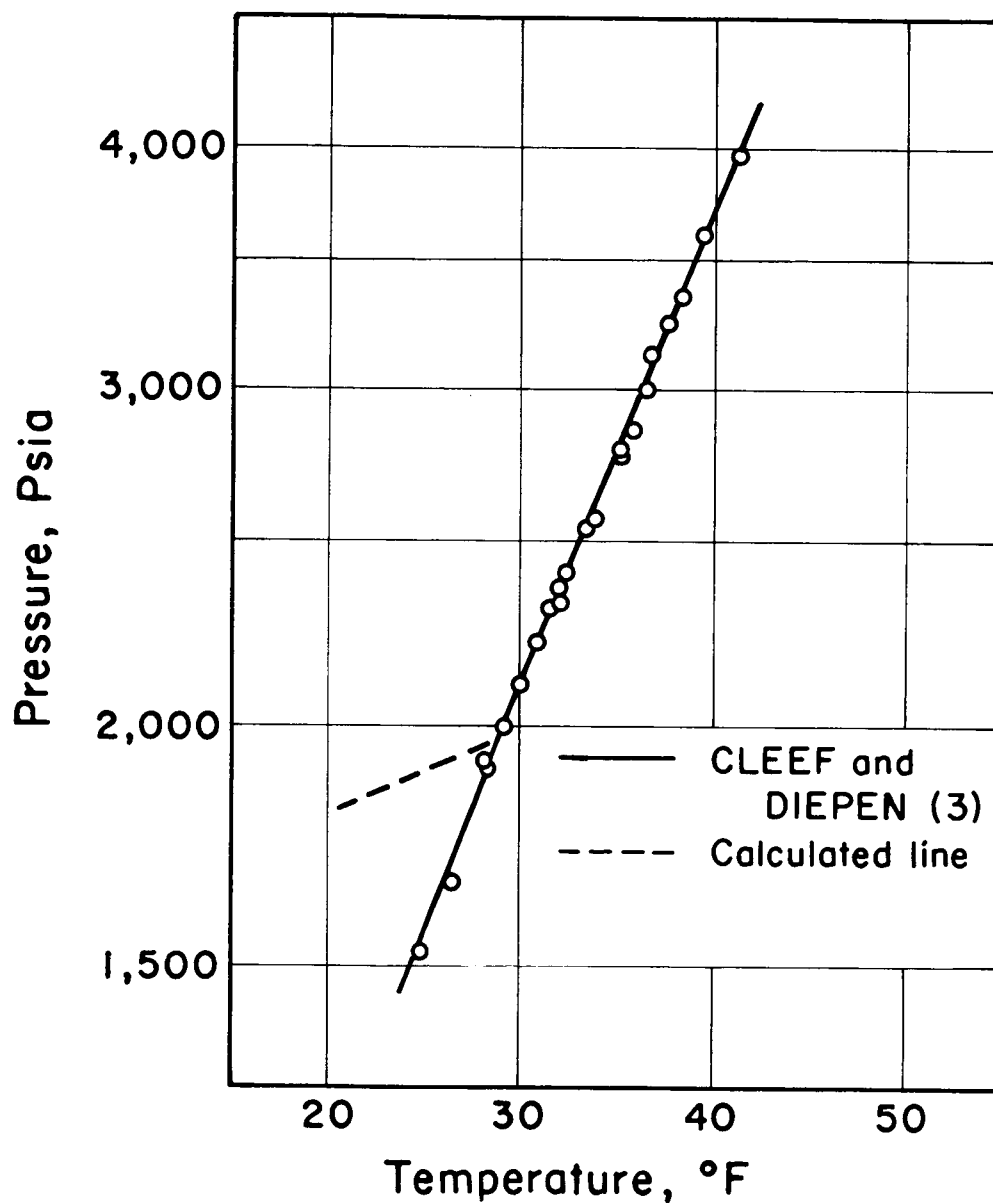


FIG. 7 - POTENTIAL FIELDS WITHIN ARGON HYDRATE CAGES





**FIG. 8 – COMPARISON BETWEEN EXPERI-  
MENTAL and CALCULATED LINES  
of NITROGEN HYDRATE**

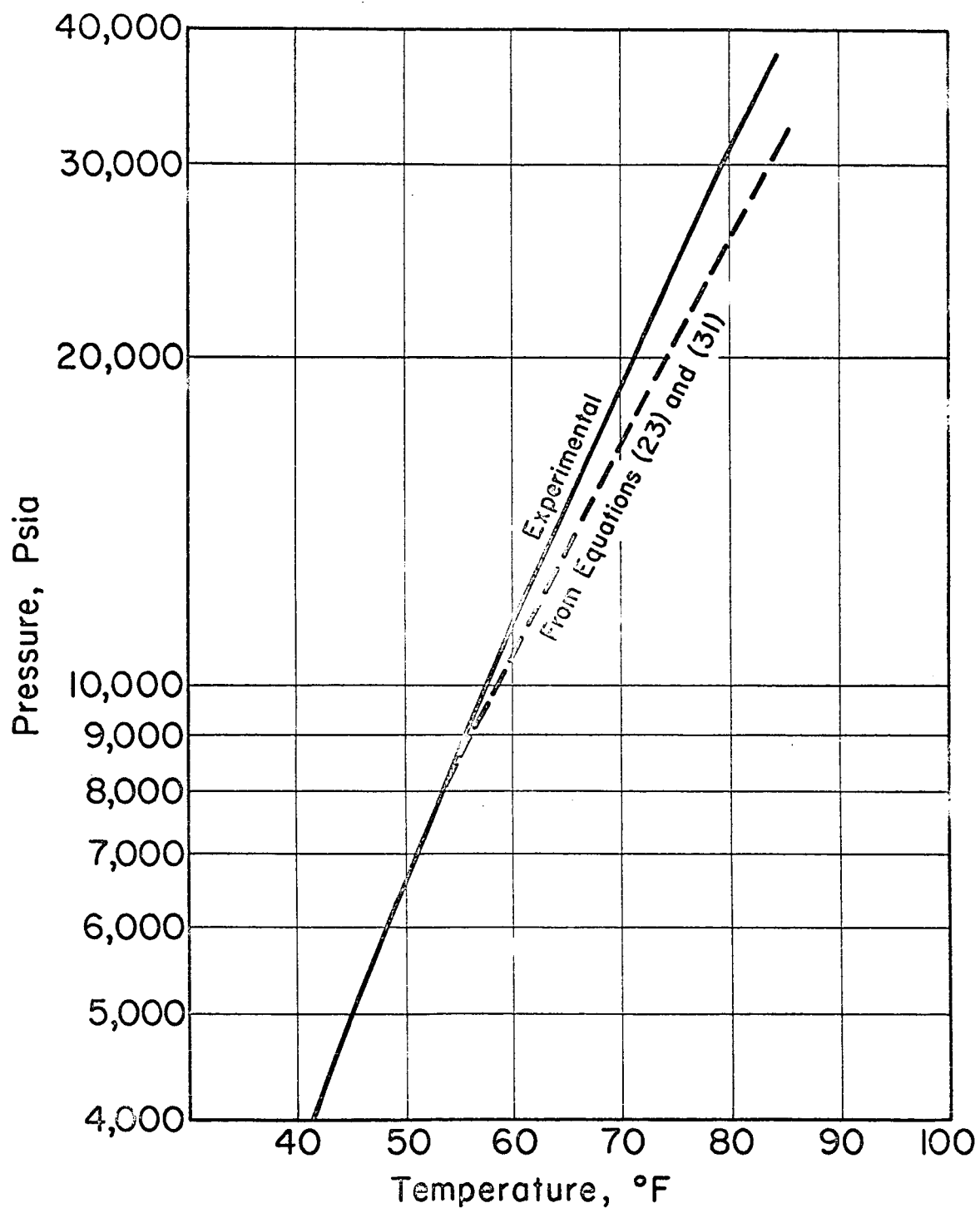


FIG. 9 - COMPARISON BETWEEN the EXPERIMENTAL and CALCULATED LINES for NITROGEN HYDRATE